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(54) Title: POLYMERISATION REGULATION

$$R^1 - \overset{\overset{\displaystyle S}{\|}}{C} - Z - R^2 \qquad (I)$$
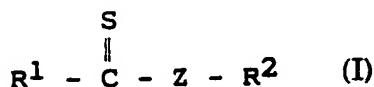
(57) Abstract

A process for the production of low molecular weight polymers by free radical polymerisation of one or more monomers in the presence of a chain transfer agent, characterized in that the chain transfer agent comprises one or more compounds of general formula (I), wherein R^1 is a hydrogen atom, an alkyl group, or a group capable of activating the vinylic carbon towards free radical addition; R^2 represents an optionally substituted alkyl, optionally substituted alkenyl, optionally substituted alkynyl, or optionally substituted satured, unsatured or aromatic carbocyclic or heterocyclic ring; and Z represents an oxygen, sulphur, phosphorus, or nitrogen atom bound to another atom or group of atoms in order to satisfy its valency.

- 1 -

POLYMERISATION REGULATION

The invention relates to processes for radical-initiated polymerisation of
unsaturated species and for the regulation of molecular weight and end-group

5   functionality of the polymeric products produced from such processes. Polymers
of limited molecular weights, or oligomers, are useful as precursors in the
manufacture of other polymeric materials and as additives or components of
formulations for plastics, elastomerics, and surface coating compositions, as well as
being useful in their own right in many applications. For example, low molecular

10   weight polymers are often required for ease of processing. End-functional
polymers are important as building-blocks for advanced copolymers. If of
sufficiently low molecular weight, end functional polymers often display useful
surface active or compatibilising properties.

15   In conventional polymerisation practice, the manufacture of low molecular weight
polymers requires the use of an initiator and a chain transfer agent. The initiator
acts as a free radical source, whereas the chain transfer agent or regulator controls
the molecular weight of the polymer molecule by reacting with the propagating
polymer radical to terminate its growth. The chain transfer agent then causes the

20   initiation of a new polymer chain thus transferring the growth process from one
discrete polymer molecule to another discrete polymer molecule. At least a part
of the chain transfer agent is incorporated into the polymer molecule and is
thereby consumed in the process.

25   The chain transfer agents most commonly used are alkanethiols which possess an
objectionable odour, lead to a wide distribution of molecular weights in batch
polymerisations with certain monomers, do not allow the production of di-end
functional polymers and have limitations as to the types of functional groups that
can be installed at the end of the polymer chain. There is also little scope with

30   thiols for the chain transfer constant to be optimised for a particular
polymerisation. In many polymerisations with thiols, the chain transfer constant, a
measure of the effectiveness of the polymerisation regulator, departs significantly

from the ideal of 1.0 that is the optimum for batch polymerisations at moderate to high conversions. The desirability of chain transfer constants close to 1.0 is reviewed by an article by T. Corner in *Advances in Polymer Science*, volume 62, p. 95 (1985). International Patent Application PCT/AU87/00412 and Australian

5   Provisional Patent Application PJ7146/89 disclose novel polymerisation processes employing regulators that help overcome many of the disadvantages of thiols, particularly in relation to chain transfer constant and, in part, provide polymerisation processes that give alternative end groups. They also allow incorporation of a wider variety of useful functional groups at the ends of polymer

10 chains.

The present invention seeks to overcome the disadvantages of polymerisations regulated with thiols by using alternative polymerisation regulators. These regulators have good stability and shelf life while maintaining many of the

15 advantages over thiols. In the majority of cases, the materials that are part of the present process present a different range of chain transfer activities, allowing more opportunity for an optimal process to be selected for a given polymerisation system of monomers and polymerisation conditions. The chain transfer constant that a given regulator possesses is an important consideration in selecting the

20 optimum process for producing low molecular weight polymers.

The present invention provides a process for the production of low molecular weight polymers by free radical polymerisation, which process is characterised by the addition to the polymerisation system of a compound of the general formula I

25

$$R^1 - \overset{\displaystyle S}{\underset{\displaystyle \|}{C}} - z - R^2 \qquad\qquad (I)$$

30 wherein
R^1 is a hydrogen atom, an alkyl group, or preferably, a group capable of activating the vinylic carbon towards free radical addition;

R^2 represents an optionally substituted alkyl, optionally substituted alkenyl,

optionally substituted alkynyl, or optionally substituted saturated, unsaturated or aromatic carbocyclic or heterocyclic ring; and

Z represents an oxygen, sulphur, phosphorus, or nitrogen atom bound to another
5   atom or group of atoms in order to satisfy its valency.

Suitable groups for R^1 are optionally substituted phenyl or other optionally substituted aromatic groups, alkoxycarbonyl or aryloxycarbonyl (-COOR), carboxy (-COOH), acyloxy (-O_2CR), carbamoyl (-CONR_2), and cyano (-CN), where R is an
10   alkyl or aryl group.

Optional substituents for R^1 and/or R^2 in formula I may comprise either reactive or non-reactive groups. "Reactive substituent groups" are groups which do not . take part in the actual lowering of the molecular weight but are installed at the
15   ends of the polymer chains and may be capable of subsequent chemical reaction. The low molecular weight polymer containing such a reactive group or groups is thereby able to undergo further chemical transformation, such as being joined with another polymer chain. Suitable reactive substituents include hydroxy (-OH), amino (-NH$_2$), halogen, allyl, cyano, epoxy, and carboxylic acid and its derivatives,
20   such as ester groups (-COOAlkyl). "Non-reactive substituent groups" may be any groups which are not deleterious to the polymerisation reaction or product, for example, alkoxy (-OAlkyl) or alkyl groups.

Substituted rings may have their reactive substituent groups directly attached to
25   the ring or indirectly attached by means of a methylene group or other side chain.

Alkyl groups referred to in this specification may contain from 1 to 32 carbon atoms. Alkenyl and alkynyl groups may contain from 2 to 32 carbon atoms. Saturated, unsaturated, or aromatic carbocyclic or heterocyclic rings may contain
30   from 3 to 14 atoms.

The process of this invention may be adopted by the users of conventional

- 4 -

processes using thiols with little change to reaction conditions other than the substitution of the appropriate quantity of a compound of general formula I for the thiol. The proportion of the compound of general formula I used may be in the range of 0.01 to 30 mole percent based on total monomer, with a preferred

5   range 0.1 to 5 mole percent. The process may be operated at any of the reaction conditions appropriate to free radical polymerisation, i.e. temperatures from - 100°C to 400°C and pressures from below atmospheric to 3000 atmospheres. Bulk, solution, emulsion, suspension or other conventional polymerisation modes may be used. Any unsaturated monomers susceptible to free radical

10   polymerisation may be used although it should be noted that the chain transfer constant will vary with the monomer used. Suitable unsaturated monomers include acrylic esters, methacrylic esters, acrylonitrile, vinyl halides, vinyl esters, vinyl aromatics, unsaturated or poly unsaturated hydrocarbons, or mixtures of these. For example, the process is applicable to the manufacture of synthetic

15   rubbers, and other polymer formulations where reduced molecular weight aids processing and improves properties. The process can also be used to produce low molecular weight polymers and oligomers for a variety of applications such as high-solids surface coatings, paints, and adhesives.

20   Compounds of general formula I are readily prepared and, unlike the lower molecular weight thiols, they do not possess an objectionable odour. The compounds used in the process of this invention display an unexpected high activity in controlling molecular weight in polymerisation reactions and have chain transfer constants that may be superior to those of thiols, particularly with styrene

25   and acrylates. Their activity is such that their chain transfer constants can approach the optimum of 1.0 for batch polymerisations and this activity is not as highly dependent as that of thiols on the structure of the propagating radical.

     A feature of the process of this invention is that, unlike processes described in

30   many of the examples of International Patent Application PCT/AU87/00412, it produces polymer chains that do not contain terminal unsaturation. In addition, those chain transfer agents described in International Patent Application

- 5 -

PCT/AU87/00412 that specifically do not introduce terminal unsaturation (for example, α-benzyloxystyrene and derivatives) have less satisfactory chain transfer constants and lower shelf life than the compounds of formula I.

5   An additional, unique feature of the process is that the resulting polymers can be hydrolysed to give a terminal thiol group. Such hydrolysis cleaves off the residue of the chain transfer agent containing R^1 and therefore there is no need for R^1 to contain a functional substituent for the production of thiol terminated polymers. If R^2, however, contains a functional substituent, a di-end functional polymer will

10   be the product of the process (after the hydrolysis step) and one of the end groups will be a thiol group. Thiol terminated polymers have application as odour-free polymeric chain transfer agents and as building blocks for the preparation of block and graft copolymers.

15   The end functional polymers produced by any of the aspects of the process described above can be converted into polymers with different end functionality by chemical reaction as is well known in the art. For example, hydroxy terminated polymers can be converted into macromonomers by reaction with methacryloyl chloride. These macromonomers are useful materials for the preparation of graft

20   copolymers by free radical copolymerisation.

The materials of formula I that are employed in the process of this invention may be prepared by reaction of the corresponding O-ester with Lawesson's reagent or by treatment of alcohols or alkoxides with thiobenzoyl chloride or the sodium salt

25   of (thiobenzylthio)acetic acid. The reaction of iminoesters with hydrogen sulfide has also been reported to give thionoesters.

$$
CH_3O\!-\!\!\underset{\underset{\displaystyle -}{\overline{}}}{\overline{\overline{}}}\!\!\underset{S}{\overset{S}{\,}}\!\!-\!P\!\!\underset{S}{\overset{S}{\,}}\!\!P\!-\!\!\underset{\underset{\displaystyle =}{\overline{}}}{\overline{}}\!\!-OCH_3
$$

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Lawesson's Reagent

SUBSTITUTE SHEET

- 6 -

The following illustrates some of the methods used to prepare examples of the compounds used in the process.

Benzyl thionobenzoate:

5   *By method A [Lawesson's reagent].* Benzyl benzoate (2.1 g) was heated at 140 °C for 24 h with Lawesson's Reagent (4.9 g) in anhydrous xylene (10 ml). After removal of the solvent and subjection of the mixture to chromatography on silica gel and recrystallization from pentane at low temperature, benzyl thionobenzoate was obtained in 67% yield. ^{1}H NMR (CDCl$_3$): δ = 5.64 (s, 2H), 7.3-8.2 (m, 10H).

10

By method B [Thionobenzoyl chloride route]. Thionyl chloride (71 g) was added dropwise to a solution of dithiobenzoic acid (47 g) in anhydrous ether (44 ml). After 7 h of stirring at ambient temperature, the ether and excess thionyl chloride were removed under reduced pressure. The residue was then distilled twice to

15   afford the thioacid chloride (61%): b.p. 54-64 °C [0.01 mmHg]. Triethylamine (2.03 g) was added in one portion to a solution of the thioacid chloride (3.13 g) and benzyl alcohol (2.16 g) in dry acetone (40 ml) under nitrogen with vigorous stirring. The stirring was continued for 15 h at ambient temperature. The mixture was then poured into water and extracted with ether. The extracts were

20   washed and dried (MgSO4) and the residue was subjected to chromatography on silica gel (eluent: hexane) to give a viscous yellow oil (3.0 g) which was crystallised from pentane to afford benzyl thionobenzoate (2.4 g, 53%): m.p. 39-40 °C.

By method C [(Thiobenzylthio)acetic acid route]. Phenylmagnesium bromide was

25   prepared by adding bromobenzene (20 g) in ether (100 ml) dropwise under nitrogen and reflux to a stirred mixture of magnesium turnings (3.2 g) in anhydrous ether (50 ml). After 30 minutes boiling under reflux, the mixture was cooled in ice and carbon disulfide (12 ml) was added dropwise. The mixture was allowed to warm gradually to 20 °C and stirred for a further 15 h. After this

30   period, ice (130 g) was cautiously added, and the organic layer was separated. The sodium salt of chloroacetic acid (12 g) was added to th aqueous phase and the mixture was allowed to stand for 24 h. After this period, it was brought to pH

1 with hydrochloric acid and extracted with ether. The ether extracts were washed
with water (x 3), dried (CaCl$_2$), and the solvent was removed to afford a residue
that was recrystallised from benzene to give the acid derivative (7.9 g): m.p. 125-
126 °C). A portion (1.06 g) was dissolved in dry tetrahydrofuran (125 ml) and

5   sodium hydride (0.48 g) was then added. After the effervescence had ceased,
imidazole (0.68 g) was added and the mixture was refluxed for 5 minutes. Benzyl
alcohol was then added and the mixture was refluxed for a further 5 min. It was
then cooled, poured into water, and extracted with ether. The extracts were
washed three times with water, dried and the solvent was removed to give benzyl

10   thionobenzoate (0.72 g), which was further purified by flash chromatography on
silica gel (eluent: b.p. 40-60 °C petroleum spirit) and recrystallization from
pentane. Yield: 4 g. m.p. 38-39 °C.

(4-Methoxycarbonylbenzyl) thionobenzoate: Method C was used to prepare this

15   compound in low yield (ca. 5% overall) from bromobenzene and methyl (4-
hydroxymethyl)benzoate. The thionoester was recrystallised from
dichloromethane/hexane: m.p. 90-91 °C. ^{1}H NMR (CDCl$_3$): δ = 3.92 (s, 3H), 5.74
(s, 2H), 7.2-7.7 (m, SH), 7.9-8.3 (m, 4H). MS (CH^4): m/z 287 (MH$^+$, 25%),149
(32%).

20

Benzyl 4-methoxythionobenzoate: This compound was prepared from 4-
bromoanisole and benzyl alcohol in 5% overall yield by *Method C*. It was
recrystallised from dichloromethane/hexane: m.p. 68-69 °C. ^{1}H NMR (CDCl$_3$): δ
= 3.67 (s, 3H), 5.60 (s, 2H), 6.73 (d, J = 9 Hz, 2H), 7.1-7.6 (m, 5H), 8.13 (d, J =

25   9 Hz, 2H). MS (CH^4): m/z 259 (MH$^+$, 10%),135 (100%), 107 (10%), 91 (45%).

(4-Methoxycarbonylbenzyl) 4-methoxythionobenzoate: Method C was used to prepare
this compound in 11% overall yield from 4-bromoanisole and methyl (4-
hydroxymethyl)benzoate. The crude product was subjected to flash

30   chromatography (eluent: dichloromethane) and recrystallised from
dichloromethane/hexane: m.p. 83-85 °C. ^{1}H NMR (CDCl$_3$): δ = 3.83 (s, 3H), 3.93
(s, 3H), 5.75 (s, 2H), 6.83 (d, J = 7.5 Hz, 2H), 7.50 (d, J = 7.5 Hz, 2H), 7.9-8.3

- 8 -

(m, 4H). MS (CH^4): m/z 317 (MH$^+$, 3%), 149 (18%), 135 (100%). Accurate
mass m/z 317.0836. C$_{17}$H$_{17}$O$_4$S requires m/z 317.0847.

(4-Ethoxycarbonylbenzyl) 4-methoxythionobenzoate: This compound was prepared
5 from 4-bromoanisole and ethyl (4-hydroxymethyl)benzoate by *Method C.* The
overall yield was 18% and recrystallization from dichloromethane/hexane was
used for purification. m.p. 75-77 °C. ^{1}H NMR (CDCl$_3$): δ = 1.40 (t, J = 7 Hz,
3H), 3.83 (s, 3H), 4.37 (q, J = 7 Hz, 2H), 5.73 (s, 2H), 6.80 (d, J = 7.5 Hz, 2H),
7.50 (d, J = 7.5 Hz, 2H), 8.0-8.4 (m, 4H). MS (CH^4): m/z 331 (MH$^+$, 40%),163
10 (40%),135 (100%).

4-(Hydroxymethyl)benzyl thionobenzoate: This compound was prepared using
Method B in 26% yield from thiobenzoyl chloride and 1,4-benzenedimethanol. ·
After recrystallization from hexane, yellow needles of the thionoester were
15 obtained. m.p. 80-80.5 °C. ^{1}H NMR (CDCl$_3$): δ = 1.67 (s, 1H), 4.68 (s, 2H), 5.68
(s, 2H), 7.40 (m, 7H), 8.17 (d, J = 6 Hz, 2H). MS (EI): m/z 257 (M$^+$-1, 12%),
241 (90%), 121 (100%). Accurate mass m/z 258.0732. C$_{15}$H$_{14}$O$_2$S requires m/z
258.0714.

20 The following non-limiting examples illustrate the invention.

EXAMPLE 1
Preparation of Low Molecular Weight Polystyrene with Benzyl Thionobenzoate

25 Azobisisobutyronitrile (35 mg) was dissolved in freshly distilled styrene (25 ml).
Aliquots (5.0 ml) were removed and added to ampoules containing the amount of
benzyl thionobenzoate shown below in Table 1. The mixtures were polymerised at
60 °C for 1 h in the absence of oxygen. The contents of the ampoule were then
poured into methanol and the precipitated polymer was collected and dried *in*
30 *vacuo* overnight. A small portion was examined by gel permeation
chromatography (GPC) using a Waters Instrument connected to six µ-Styragel
columns (10^6, 10^5, 10^4, 10^3, 500, and 100 Å pore size). Tetrahydrofuran was used

SUBSTITUTE SHEET

- 9 -

as eluent at a flow rate of 1 ml/min and the system was calibrated using narrow distribution polystyrene standards (Waters). The results appear in Table 1.

Table 1

Amount of benzyl thionobenzoate added	Conversion %	$\bar{M}_n$
81 mg	2.7	11400
41 mg	2.9	20800
21 mg	3.0	37600
0 mg	3.2	124000

The chain transfer constant (C_x), calculated from these data, was 1.0 which compares favourably with that from n-butanethiol (C_x = 21-25). These results show that the compound is an efficient chain transfer agent and that the process produces polymers of low molecular weight in a controlled manner.

EXAMPLE 2

Preparation of Low Molecular Weight Poly(methyl acrylate) with Benzyl Thionobenzoate

Azobisisobutyronitrile (9 mg) was dissolved in freshly distilled methyl acrylate (25 ml). Aliquots (2.0 ml) were removed and added to ampoules containing thiophen-free benzene (8 ml) and the amount of benzyl thionobenzoate shown below in Table 2. The mixtures were polymerised at 60 °C for 1 h in the absence of oxygen. The volatiles were then removed and the polymers were dried *in vacuo* to constant weight and then examined as before. The results appear in Table 2.

- 10 -

Table 2

Amount of benzyl thionobenzoate added	Conversion %	$\bar{M}_n$ *
50 mg	3.8	9020
26 mg	6.0	17700
12 mg	9.2	35600
0 mg	16	473000

* Polystyrene-equivalent number average molecular weight, obtained by GPC.

The chain transfer constant (C_x), calculated from these data, was 1.2, which compares favourably with that from n-butanethiol (C_x= 1.7).

EXAMPLE 3

Preparation of Low Molecular Weight Poly(vinyl acetate) with Benzyl Thionobenzoate

Azobisisobutyronitrile (16 mg) was dissolved in freshly distilled vinyl acetate (100 ml). Aliquots (10.0 ml) were removed and added to ampoules containing the amount of benzyl thionobenzoate shown below in Table 3. The mixtures were polymerised at 60°C for 1 h in the absence of oxygen. The volatiles were then removed and the polymers were dried *in vacuo* to constant weight and then examined as before. The results appear in Table 3.

- 11 -

Table 3

Amount of benzyl thionobenzoate added	$\overline{M}_n$ *
2.2 mg	1900
0	253000

* Polystyrene-equivalent number average molecular weight, obtained by GPC.

The chain transfer constant (C_x), calculated from these data, was >20. These results show that the compound acts as a very active regulator in polymerisation of vinyl acetate.

EXAMPLE 4

Preparation of Low Molecular Weight Polystyrene with (4-Methoxycarbonylbenzyl) Thionobenzoate

Samples of polystyrene were prepared on the same scale and in the manner of example 1. The amount of (4-methoxycarbonylbenzyl) thionobenzoate added and the results of the polymerisation are shown in Table 4.

- 12 -

Table 4

Amount of (4-methoxycarbonylbenzyl) thionobenzoate added	$\overline{M}_n$
80 mg	23000
40 mg	41900
20 mg	66300
0 mg	142000

The chain transfer constant (C_x), calculated from these data, was 0.59. A sample of low molecular weight polystyrene ($\overline{M}_n$ = 4570) prepared with (4-methoxycarbonylbenzyl) thionobenzoate was examined by ^{1}H NMR spectroscopy and showed signals at δ = 3.83 indicative of the presence of methyl ester groups. Integration of the spectrum and comparison with the integral of the aromatic styrene signal showed there to be an end group functionality of 0.9-1.0. This experiment shows that the process can be used to prepare end functional polymers.

EXAMPLE 5

Preparation of Low Molecular Weight Poly(methyl acrylate) with (4-Methoxycarbonylbenzyl) Thionobenzoate

Samples of poly(methyl acrylate) were prepared according to the directions given in Example 2, except that (4-methoxycarbonylbenzyl) thionobenzoate was used rather than benzyl thionobenzoate. The amount of (4-methoxycarbonylbenzyl) thionobenzoate added and the results of the polymerisation are shown in Table 5.

SUBSTITUTE SHEET

- 13 -

Table 5

Amount of (4-methoxycarbonylbenzyl) thionobenzoate added	$\bar{M}_n$
50 mg	7700
26 mg	14300
12 mg	28300
0 mg	772000

* Polystyrene-equivalent number average molecular weight, obtained by GPC

The chain transfer constant (C_x), calculated from these data, was 1.4, which compares favourably with that from n-butanethiol ($C_x = 1.7$).

EXAMPLE 6

Preparation of Low Molecular Weight Polystyrene with Benzyl 4-Methoxy(thionobenzoate)

Samples of polystyrene were prepared on the same scale and in the manner of example 1. The amount of benzyl 4-methoxy(thionobenzoate) added and the results of the polymerisation are shown in Table 6.

Table 6

Amount of benzyl 4-methoxy(thionobenzoate) added	$\bar{M}_n$
80 mg	65100
40 mg	93500
20 mg	113000
0 mg	145000

The chain transfer constant (C_x), calculated from these data, was 0.12.

EXAMPLE 7

Preparation of Low Molecular Weight Poly(methyl acrylate) with Benzyl 4-Methoxy(thionobenzoate)

Samples of poly(methyl acrylate) were prepared according to the directions given in Example 2, except that benzyl 4-methoxy(thionobenzoate) was used rather than benzyl thionobenzoate. The amount of benzyl 4-methoxy(thionobenzoate) added and the results of the polymerisation are shown in Table 7.

Table 7

Amount of benzyl 4-methoxy(thionobenzoate) added	$\bar{M}_n$ *
50 mg	10700
26 mg	18600
13 mg	42600
0 mg	394000

* P lystyrene-equivalent number average molecular weight, obtained by GPC

The chain transfer constant (C_x), calculated from these data, was 1.1, which compares favourably with that from n-butanethiol (C_x = 1.7).

EXAMPLE 8

5   *Preparation of Low Molecular Weight Polystyrene with 4-(Methoxycarbonyl)benzyl 4-Methoxy(thionobenzoate)*

Samples of polystyrene were prepared on the same scale and in the manner of example 1. The amount of 4-(methoxycarbonyl)benzyl 4-methoxy(thionobenzoate)
10   added and the results of the polymerisation are shown in Table 8.

Table 8

Amount of 4-(methoxycarbonyl)benzyl 4-methoxy(thionobenzoate) added	$\overline{M}_n$
81 mg	48400
40 mg	86000
20 mg	105300
0 mg	150000

The chain transfer constant (C_x), calculated from these data, was 0.25. The total average functionality (methoxy and methoxycarbonyl groups) calculated by ^{1}H NMR on a sample of polystyrene of $\overline{M}_n$ = 13300 (prepared with
25   4-(methoxycarbonyl)benzyl 4-methoxy(thionobenzoate) was 2.1, which shows that 4-(methoxycarbonyl)benzyl 4methoxy(thionobenzoate) is efficient in introducing functional groups at the termini of polymer chains and that this type of chain transfer agent can be used to prepare end-functional polymers.

30   EXAMPLE 9

Preparation of Low Molecular Weight Poly(methyl acrylate) with 4-(Methoxycarbonyl)benzyl 4-Methoxy(thionobenzoate)

- 16 -

Samples of poly(methyl acrylate) were prepared according to th directions given
in Example 2, except that 4-(methoxycarbonyl)benzyl 4-methoxy(thionobenzoate)
was used rather than benzyl thionobenzoate. The amount of
4-(methoxycarbonyl)benzyl 4-methoxy(thionobenzoate) added and the results of

5   the polymerisation are shown in Table 9.

Table 9

Amount of 4-(methoxycarbonyl)benzyl 4-methoxy(thionobenzoate) added	$\overline{M}_n$ *
50 mg	10700
26 mg	18600
13 mg	42600
0 mg	394000

* Polystyrene-equivalent number average molecular weight, obtained by GPC

The chain transfer constant (C_x), calculated from these data, was 1.1, which

20   compares favourably with that from n-butanethiol (C_x = 1.7).

EXAMPLE 10

Preparation of Low Molecular Weight Polystyrene with 4-(Ethoxycarbonyl)benzyl 4-Methoxy(thionobenzoate)

25

Samples of polystyrene were prepared on the same scale and in the manner of
Example 1. The amount of 4-(ethoxycarbonyl)benzyl 4-methoxy(thionobenzoate)
added and the results of the polymerisation are shown in Table 10.

- 17 -

Table 10

Amount of 4-(ethoxycarbonyl)benzyl 4-methoxy(thionobenzoate) added	$\bar{M}_n$
616 mg	13500
0 mg	150000

The presence of ethoxycarbonyl and methoxy end groups in the lower molecular weight sample of polystyrene was shown by signals in the ^{1}H NMR spectrum at δ = 4.28 and 3.83, respectively.

EXAMPLE 11

Preparation of Low Molecular Weight Polystyrene with 4-(hydroxymethyl)benzyl thionobenzoate

Samples of polystyrene were prepared on the same scale and in the manner of example 1. The amount of 4-(hydroxymethyl)benzyl thionobenzoate added and the results of the polymerisation are shown in Table 11.

Table 11

Amount of 4(hydroxymethyl)benzyl thionobenzoate added	$\bar{M}_n$
81 mg	25600
40 mg	43900
20 mg	59500
0 mg	113000

The chain transfer constant was 0.43. The presence of the end group shown below in a polymer of $\bar{M}n$ = 6810, prepared with 4-(hydroxymethyl)benzyl

SUBSTITUTE SHEET

- 18 -

thionobenzoate, was confirmed by a broad signal in th ^{1}H NMR spectrum at
δ = 4.4-4.7 (due to the benzyl methylene hydrogens) and an infrared absorption
at 3415 cm^{-1}.

5

$$-\!\!\!\!\bigcirc\!\!\!\!-CH_2OH$$
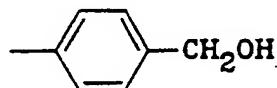
End group of polymer prepared with 4-(hydroxymethyl)benzyl thionobenzoate

10   After treatment with *t*-butyldimethylsilyl chloride and imidazole, this polymer
showed signals at δ = 0.08 in the ^{1}H NMR spectrum due to the methyls of a
t-butyldimethylsilyl ether group. The formation of this silyl ether further confirms
the presence of a hydroxyl end group.

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CLAIMS

1.   A process for the production of low molecular weight polymers by free radical polymerisation of one or more monomers in the presence of a chain

5   transfer agent, characterised in that the chain transfer agent comprises one or more compounds of the general formula I
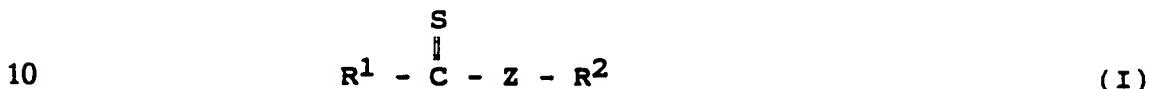
$$
\underset{R^1 - C - Z - R^2}{\overset{\overset{\textstyle S}{\textstyle \|}}{}} \qquad (I)
$$

10

wherein
R^1 is a hydrogen atom, an alkyl group, or a group capable of activating the vinylic carbon towards free radical addition;

15

R^2 represents an optionally substituted alkyl, optionally substituted alkenyl, optionally substituted alkynyl, or optionally substituted saturated, unsaturated or aromatic carbocyclic or heterocyclic ring; and

20   Z represents an oxygen, sulphur, phosphorus, or nitrogen atom bound to another atom or group of atoms in order to satisfy its valency.

2.   A process as claimed in Claim 1, characterised in that R^1 is a substituted phenyl or other optionally substituted aromatic group, or an alkoxycarbonyl or

25   aryloxycarbonyl, carboxy, acyloxy, carbamoyl, or cyano group.

3.   A process as claimed in Claim 1 or Claim 2, characterised in that R^1 and/or R^2 in formula I have one or more reactive substituent groups which do not take part in the actual lowering of the molecular weight but are installed at the

30   ends of the polymer chains and may be capable of subsequent chemical reaction, whereby the low molecular weight polymer product containing the reactive group or groups is thereby able to undergo further chemical transformation.

4.   A process as claimed in Claim 3, characterised in that the reactive

SUBSTITUTE SHEET

- 20 -

substituent group is an hydroxy, amino, halogen, allyl, cyan , epoxy, or carboxylic acid group or a derivative of a carboxylic acid group.

5.   A process as claimed in any one of the preceding Claims, characterised in

5   that the compound of general formula I is added to present in an amount of from 0.01 to 30 mole percent based on total monomer.

6.   A process as claimed in any one of the preceding Claims, characterised in that the monomer is selected from the groups consisting of acrylic esters,

10   methacrylic esters, vinyl esters, vinyl aromatics, unsaturated or poly unsaturated hydrocarbons, or mixtures of any two or more of such monomers.

7.   A process as claimed in any one of the preceding Claims, characterised in that the resulting polymer is hydrolysed to give a terminal thiol group.

15

INTERNATIONAL SEARCH REPORT

I.	CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent classification (IPC) or to both National Classification and IPC

Int. Cl.[5] C08F 002/38, C07C 327/26

II.	FIELDS SEARCHED

Minimum Documentation Searched [7]

Classification System	Classification Symbols
IPC	C08F 002/38, C08F 001/80

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched [8]

AU: IPC as above; Australian Classification 09.4-33, 09.4-35

III.	DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category[*]	Citation of Document, [11] with indication, where appropriate of the relevant passages [12]	Relevant to Claim No [13]
X	EP,A, 407059 (JAPAN SYNTHETIC RUBBER CO LTD) 9 January 1991 (09.01.91). Refer to page 3, page 6 lines 1-19, page 13 lines 45-55, page 19 table 1 and claim 1	1, 3, 5-7
X	WO,A, 89/10371 (NORSOLOR) 2 November 1989 (02.11.89). Refer to the abstract	1, 3, 5-7
X	US,A, 4054731 (MARUBASHI et al) 18 October 1977 (18.10.77). Refer to column 2 lines 9-48, column 3 line 44-column 4 line 16, column 5 line 43-column 6 line 11, example 1 and claim 1	1, 3, 5-7
X	US,A, 3838140 (MAYER-MADER, BOLDT) 24 September 1974 (24.09.74). Refer to column 1 and column 2, example II and claim 1	1, 3, 5-7

*	Special categories of cited documents : [10]	"T"	Later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	Document defining the general state of the art which is not considered to be of particular relevance		
"E"	earlier document but published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior t the international filing date but later than the priority date claimed		
		"&"	document member of the same patent family

IV.	CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
1 May 1992 (01.05.92)	13 May 1992 (13.05.92)

International Searching Authority	Signature of Authorized fficer
AUSTRALIAN PATENT OFFICE	M BREMERS

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

V. ☐ **OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE** [1]

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claim numbers ..., because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claim numbers ..., because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claim numbers ..., because they are dependent claims and are not drafted in accordance with the second and third sentences of PCT Rule 6.4a

VI. ☐ **OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING** [2]

This International Searching Authority found multiple inventions in this international application as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.

2. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:

3. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

4. ☐ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest

☐ The additional search fees were accompanied by applicant's protest.

☐ No protest accompanied the payment of additional search fees.